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THE CONFIGURATIONAL PARTITION

FUNCTIONS OF SOLID SOLUTIONS

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Abstract

This short paper applies a method for studying the
configurational partition function of regular solutions
developed by Wang, Hsu and the author to a number of special
cases. In such concrete calculations it is seen that the
method is applicable to almost every type of solid solutions.
In fact, its applicability is independent of the type of
lattice which atoms of the solution inhabit, of the existence
of the long distance order, of the existence of interactions
between atoms more distant than nearest neighbours, and of
the number of components in the solution. Since the method
is actually an expansion of the configurational free energy
in terms of certain coordination numbers of the lattice,
the results of the calculations after ignoring the higher
coordination numbers become closed expressions in terms of
the Boltzmann factors and thus avoid expansions in kT or in
$(kT)^{-1}$. Needless to say, expansion of the results obtained
here in $(kT)^{-1}$ gives results identical with those obtained
by Kirkwood's method.

Next we discuss quasi-chemical formulas based on the
above method. We point out that if we neglect all the co-
ordination numbers except the lowest, we obtain the usual
quasi-chemical formula, quite independently of the number of
components in the solution. (A corresponding combinatory
formula is derived.) On including higher coordination
numbers, we get natural extensions of the quasi-chemical
formula. Thus for a binary solid solution on a face centered
cubic system, the quasi-chemical formula after including the
next higher coordination number becomes

$$X_{AA} = X'_{AA} + 3X'' \begin{pmatrix} A \\ AA \end{pmatrix} + 3X'' \begin{pmatrix} A \\ AB \end{pmatrix},$$

$$X_{AB} = 2X'_{AB} + 6X'' \begin{pmatrix} A \\ AB \end{pmatrix} + 6X'' \begin{pmatrix} A \\ BB \end{pmatrix},$$

$$X_{BB} = X'_{BB} + 3X'' \begin{pmatrix} A \\ BB \end{pmatrix} + 3X'' \begin{pmatrix} B \\ BB \end{pmatrix},$$

$$\frac{(X'_{AB})^2}{X'_{AA}X'_{BB}} = \frac{\left[X'' \begin{pmatrix} A \\ AB \end{pmatrix}\right]^2}{X'' \begin{pmatrix} A \\ AA \end{pmatrix} X'' \begin{pmatrix} A \\ BB \end{pmatrix}} = \frac{\left[X'' \begin{pmatrix} A \\ BB \end{pmatrix}\right]^2}{X'' \begin{pmatrix} A \\ AB \end{pmatrix} X'' \begin{pmatrix} B \\ BB \end{pmatrix}} =$$

$$= \exp\{-2 V_{AB} - V_{AA} - V_{BB})/kT\}, \qquad (2)$$

$$(X'_{AA} + X'_{AB}) = -18 N \theta_A,$$

$$(X'_{AB} + X'_{BB}) = -18 N \theta_B, \qquad (3)$$

$$X'' \begin{pmatrix} A \\ AA \end{pmatrix} + 2X'' \begin{pmatrix} A \\ AB \end{pmatrix} + X'' \begin{pmatrix} A \\ BB \end{pmatrix} = 8 N \theta_A,$$

$$X'' \begin{pmatrix} B \\ BB \end{pmatrix} + 2X'' \begin{pmatrix} A \\ BB \end{pmatrix} + X'' \begin{pmatrix} A \\ AB \end{pmatrix} = 8 N \theta_B. \qquad (4)$$

In the above, $N\theta_A, N\theta_B$ denote the numbers of A, B atoms, $X'_{AA}, X'_{AB}, \cdots, X'', \cdots$ are numbers determined by (2), (3), (4), and their substitution into the righthand sides of (1) gives the numbers X_{AA}, X_{AB}, X_{BB} of AA, AB, BB pairs of nearest neighbours. It may be noted that X' may be negative and they do not bear any direct physical significance. It is also pointed out that instead of considering the numbers of pairs of nearest neighbours, we may consider directly the numbers of pairs of triplets (ie. 3 atoms forming mutually nearest neighbours) and write down by analogy (to the usual quasi-chemical formula) new quasi-chemical equations for the different numbers of triplets. (From this, a combinatory formula is easily derived). It is shown that such a theory differs from (1) - (4) given above.

This short paper consists of two parts. The first part discusses the application of the method of finding the configurational partition functions of solid solutions, which was developed by Wang Te-mao, Hsu Yung-Huan, and the author (1) to different solid solutions. Comparisons have been made of the results obtained to the corresponding ones obtained by the method of Kirkwood.(2,3,4,5) We discuss the following cases:

(1) AB-type crystal lattice; binary solid solution
(2) Face-centered crystal lattice; binary solid solution
(3) AB-type crystal lattice binary solid solution with interaction between next nearest neighbors.

Essentially, this method takes advantage of the property that the logarithm of the configurational partition function, F, is a linear combination of certain coordination numbers of the crystal lattice. After ignoring the higher coordination numbers of the lattice, we obtain F as a closed expression, no longer requiring a series expansion in $(KT)^{-1}$ or (KT). Therefore, we expect the result thus obtained to be correct for any temperature. And we can compare the result to that by the Kirkwood method by simply expanding the result into series in $(KT)^{-1}$. The results should be the same, and in fact, they are.

In the second part, we use the method of reference 1 to discuss the quasi-chemical approximation. First we point out that if the lowest coordination number is retained, the conventional quasi-chemical approximation formulas are correct no matter how many kinds of atoms there are in the solid solution. Second, we point out how to improve the conventional quasi-chemical formula by keeping higher coordination numbers.

PART I

(1) AB-type lattice binary solid solution.

For a binary solid solution with the AB-type lattice, we assume that the total number of atoms is N, the number of A atoms is $N\theta$, and interaction exists only for atoms forming nearest neighbor pairs. According to reference 1, we can prove that the logarithm of the configurational partition function, F, is

$$\log\binom{N}{N\theta} + (\Sigma\lambda_{cc'})f_1(N,\theta,T) +$$
$$+ (\Sigma\lambda_{cc'}\lambda_{cc''}\lambda_{c'''c'}\lambda_{c'''c''})f_2(N,\theta,T) + \cdots, \qquad (1)$$

in which $\lambda_{cc'}$ is the neighbor matrix, defined as

$$\lambda_{cc'} = 1, \qquad \text{if } c, c' \text{ are nearest neighbors}$$
$$= 0, \qquad \text{otherwise,}$$

and the coefficients of f_1, f_2 ...., etc., are the matrix elements of the irreducible products of the λ's summed over the indices, and are called coordination numbers. The functions f_1, f_2, ... are certain functions of N, θ, and T.

Because these coordination numbers are apparently directly proportional to N, therefore f does not contain N. Reference 1 indicated that in order to determine f_1, f_2, ..., etc., we need consider only the F of a hypothetical solid solution with the same values of N and θ.

Now we are going to consider the following hypothetical lattice: the total number of points N of the hypothetical lattice are divided into N/2 groups, each group having two points and forming a nearest-neighbor pair with no nearest neighbor between groups.

Then

$$F = \frac{1}{2} N \log(1 + 2\lambda + \lambda^2 \xi) - N\theta \log \lambda, \qquad (2)$$

in which

$$\xi = \exp(-V_{AA}/kT)$$

(V_{AB}, V_{BB} assumed to be zero), is a function of N, θ, and T, determined by

$$\partial F / \partial \lambda = 0 \qquad (3)$$

From (3) we obtain

$$\frac{1}{\lambda} = \frac{1-\theta}{\theta} + \frac{1}{2\theta}(H-1), \qquad (4)$$

$$H = +\{1 + 4\theta(1-\theta)\eta\}^{1/2},$$

$$\eta = \xi - 1.$$

Substituting into (2), we get

$$N^{-1}F = -\theta \log \theta - (1-\theta)\log(1-\theta) + \frac{1}{2}\log\left(\frac{1}{2} + \eta\theta + \frac{1}{2}H\right) -$$

$$- (1-\theta)\log\left\{1 + \frac{1}{2(1-\theta)}(H-1)\right\}. \qquad (5)$$

Since for this hypothetical lattice

$$\sum \lambda_{cc'} = N, \qquad \sum \lambda_{cc''}\lambda_{cc''}\lambda_{c''c'}\lambda_{c''c''} = 0, \cdots,$$

we have

$$f_1(\theta, T) = \frac{1}{2}\log\left(\frac{1}{2} + \eta\theta + \frac{1}{2}H\right) -$$

$$- (1-\theta)\log\left\{1 + \frac{1}{2(1-\theta)}(H-1)\right\}. \qquad (6)$$

Expanding with respect to γ, we have

$$\frac{1}{2}\theta^2\eta+\frac{1}{4}\theta^2(\theta^2-2\theta)\eta^2+\frac{1}{6}[\theta^2+\theta^4(1-\theta)^2(-1-2\theta+2\theta^2)]\eta^3+$$

$$+\frac{1}{8}[-\theta^2+\theta^4(1-\theta)^2(1+2\theta+3\theta^2-10\theta^3+5\theta^4)]\eta^4+\cdots. \qquad (7)$$

To see the symmetry between θ and $(1-\theta)$, we rewrite the above expression as

$$\frac{1}{2}\theta^2\log\xi+\frac{1}{4}\theta^2(1-\theta)^2\eta^2+\frac{1}{6}\theta^2(1-\theta)^2[\theta^2+(1-\theta)^2-2]\eta^3+$$

$$+\frac{1}{8}\theta^2(1-\theta)^2\left[\frac{5}{2}\theta^4+\frac{5}{2}(1-\theta)^4-6\theta^2-6(1-\theta)^2+\frac{9}{2}\right]\eta^4+\cdots. \qquad (8)$$

To determine f_2, we consider the following hypothetical lattice: the total points N of the assumed lattice are divided into N/-1 groups, each group consisting of four points sitting on the four vertices of a cubic lattice, each side of the cubic lattice representing one nearest-neighbor pair; and, as in the former case, no nearest-neighbor pair exists between groups.

Under this condition,

$$F=\frac{1}{4}N\log(1+4\lambda+4\lambda^2\xi+2\lambda^2+4\lambda^3\xi^3+\lambda^4\xi^4)-N\theta\log\lambda. \qquad (9)$$

where λ satisfies

$$\partial F/\partial\lambda=0, \qquad (10)$$

exactly as in the former case. Equation (10) is of the fourth order in λ, and we can solve this equation analytically for λ and then substitute it into expression (9). When γ assumes its minimum value, the solution of Equation (10) is

$$\frac{1}{\lambda}=\frac{1-\theta}{\theta}+2(1-\theta)\eta-\theta(1-\theta)(1-2\theta)\eta^2+$$

$$+2\theta^2(1-\theta)^3(1-2\theta)\eta^3+\cdots, \qquad (11)$$

Substituting into expression (9),

$$N^{-1}F=-\theta\log\theta-(1-\theta)\log(1-\theta)+\theta^2\eta+\frac{1}{2}\theta^2(\theta^2-2\theta)\eta^2+$$

$$+\frac{1}{3}[\theta^2+\theta^2(1-\theta)^2(-1-2\theta+2\theta^4)]\eta^3+$$

$$+\frac{1}{4}[-\theta^2+\theta^2(1-\theta)^2(1+2\theta+4\theta^2-12\theta^3+6\theta^4)]\eta^4+\cdots. \qquad (12)$$

Since for this hypothetical lattice

$$\sum \lambda_{cc'} = 2N, \quad \sum \lambda_{cc'} \lambda_{cc''} \lambda_{c'''c'} \lambda_{c'''c''} = 2N, \quad \sum (\cdots) = 0, \cdots,$$

therefore,

$$N^{-1}F = -\theta \log \theta - (1-\theta)\log(1-\theta) + 2f_1(\theta, T) + 2f_2(\theta, T). \tag{13}$$

Comparing with (12), and making use of the known f, [see expression (7)], we arrive at

$$f_2 = \frac{1}{8}\theta^4 (1-\theta)^4 \eta^4 + \cdots. \tag{14}$$

Substituting f_1 and f_2 into expression (1), we obtain the F for all the other f's neglected. If we expand this result as a series in $(-V_{AA}/kT)^{-1}$, it appears exactly the same as the result by Kirkwood's method. (3) [In making the comparison, we neglected O $(kT)^{-6}$.]

(2) Face-centered lattice binary solid solution

Here

$$F = \log \binom{N}{N\theta} + (\sum \lambda_{cc'})f_1 + (\sum \lambda_{cc'} \lambda_{cc''} \lambda_{c'c''})f_2 +$$
$$+ (\sum \lambda_{cc'} \lambda_{cc''} \lambda_{c'''c'} \lambda_{c'''c''})f_3 + \cdots. \tag{15}$$

Therefore, we should try to evaluate f3.

Consider the following hypothetical lattice structure; the N points of the lattice are divided into N/3 groups, each group consisting of three points sitting on the vertices of an equilateral triangle. Each side of the triangle represents one nearest-neighbor pair, and there is no interaction among atoms of different groups.

Then the logarithm of the configurational partition function, F, should be

$$\frac{1}{3}N \log (1 + 3\lambda + 3\lambda^2 \xi + \lambda^3 \xi^3) - N\theta \log \lambda, \tag{16}$$

in which λ is determined by

$$\partial F / \partial \lambda = 0$$

When η assumes small values, it is easy to find

$$\frac{1}{\lambda} = \frac{1-\theta}{\theta} + 2(1-\theta)\eta - \theta(1-\theta)(1-2\theta)\eta^2 +$$

$$+ \theta(1-\theta)^2(1-2\theta)(1+\theta)\eta^3 + \cdots,$$

$$N^{-1}F = -\theta\log\theta - (1-\theta)\log(1-\theta) + \theta^2\eta + \frac{1}{2}\theta^2(\theta^2-2\theta)\eta^2 +$$

$$+ \frac{1}{3}[\theta^3 + \theta^2(1-\theta)^2(-1-\theta+\theta^2)]\eta^3 + \cdots. \tag{17}$$

Since for this lattice system we assumed

$$\sum \lambda_{cc'} = 2N, \quad \sum \lambda_{cc'}\lambda_{cc''}\lambda_{c'c''} = 2N, \quad \sum \lambda\lambda\lambda\lambda = 0, \cdots,$$

therefore

$$N^{-1}F = -\theta\log\theta - (1-\theta)\log(1-\theta) + 2f_1 + 2f_3. \tag{18}$$

Comparing with expression (17), and making use of the known f_1, we arrive at

$$f_3 = \frac{1}{6}\theta^3(1-\theta)^3\eta^3 - \theta^4(1-\theta)^4\eta^4 + \cdots. \tag{19}$$

Substituting f_1, f_2, and f_3 into (15), we would obtain immediately the expression of F with all the other f's neglected. If we expand this result into a series in $(kT)^{-1}$, we see that it is identical with that obtained by the Kirkwood method. /In making the comparison, O $(kT)^{-5}$ has been neglected7.

(3) AB-type crystal lattice solid solution with long-distance order.
In this case, we will describe only the method of calculation. The result apparently should be similar to that obtained before.
Denote the number of A atoms in the first sublattice by 1/2 $N\theta$ and the number of A atoms in the second sublattice by 1/2 $N\theta'$. The points in the first sublattice are represented by a, and the points in the second by b. Then, corresponding to the values θ and θ', the logarithm of the configurational partition function should be

$$\log\binom{\frac{1}{2}N}{\frac{1}{2}N\theta}\binom{\frac{1}{2}N}{\frac{1}{2}N\theta'} + \sum\lambda_{ab}f_i(\theta,\theta',T) + \cdots. \tag{20}$$

*Note that since here f_1 is defined slightly differently from that in expression (1), we adopt the notation f_1^*. To determine f_1^*, we will consider again the hypothetical lattice system of expression (1). The logarithm of its configurational partition function, F, is

$$\frac{1}{2}N\log(1+\lambda+\lambda'+\lambda\lambda'\xi) - \frac{1}{2}N\theta\log\lambda - \frac{1}{2}N\theta'\log\lambda', \qquad (21)$$

where λ and λ' are functions of θ, θ' and T, determined by

$$\partial F/\partial\lambda = \partial F/\partial\lambda' = 0 \qquad (22)$$

From (22), we have

$$\theta = \lambda(1+\lambda'\xi)/(1+\lambda+\lambda'+\lambda\lambda'\xi), \qquad (23)$$

$$\theta' = \lambda'(1+\lambda\xi)/(1+\lambda+\lambda'+\lambda\lambda'\xi). \qquad (24)$$

From (23), we have

$$\lambda = \theta(1+\lambda')/(1-\theta)(1+\lambda'\xi), \qquad (25)$$

Substituting into (24), we get

$$\xi(1-\theta')\lambda'^2 + \lambda'[1-\theta-\theta'+\xi(\theta-\theta')] - \theta' = 0. \qquad (26)$$

Similarly, solving the equation which satisfied,

$$\xi(1-\theta)\lambda^2 + \lambda[1-\theta-\theta'+\xi(\theta'-\theta)] - \theta = 0.$$

and substituting the values of λ and λ' into expression (21) and then making use of the property of the hypothetical lattice, $\quad \Sigma\lambda_{ab} = \frac{1}{2}N, \qquad \Sigma\lambda\lambda = \Sigma\lambda\lambda\lambda\lambda = \cdots = 0,$

we could determine f_1^* $(\theta, \theta'T)$. Because the calculation is very tedious and adds nothing new in the way of results, we omit it.

(4) Binary solid solution of AB-type lattice with next-nearest neighbor interaction:

Apparently, here

$$F = \log\binom{N}{N\theta} + (\Sigma\lambda_{cc'})f_\lambda(\theta,T) + (\Sigma\mu_{cc'})f_\mu(\theta,T) +$$

$$+ (\Sigma\lambda_{cc'}\lambda_{cc''}\mu_{c'c''})f_{\mu\lambda}(\theta,T) + \cdots, \qquad (27)$$

where $\mu_{c'c''}$ represents the "next nearest neighbor" matrix, defined as

$$\mu_{c'c''}=1 \ , \quad \text{when } c', c'' \text{ are next-nearest neighbors}$$
$$=0 \ , \quad \text{otherwise},$$

and $f_{\mu\lambda}, f_{\mu\mu}$ are functions to be determined. f_λ in the above expression is the f_1 we used before.

In order to determine $f_{\mu\mu}$ and $f_{\mu\lambda}$, we will consider the following hypothetical lattice system: the lattice is divided into $N/3$ groups, each group consisting of three points sitting on the vertices of a isoceles right triangle. The two short sides represent nearest-neighbor pairs, and the diagonal represents the next-nearest-neighbor pair. Then

$$F = \frac{1}{3}N \log (1+3\lambda+\lambda^2\xi'+2\lambda^2\xi+\lambda^3\xi^2\xi') - N\theta \log\lambda, \qquad (28)$$

where ξ' denotes $\exp(-V/kT)$ constructed from the next nearest pair AA (assuming no interaction between AB, and BB) and λ is still determined by $\partial F/\partial\lambda=0$. It can be easily calculated that

$$\frac{1}{\lambda} = \frac{1-\theta}{\theta} + \frac{2}{3}(1-\theta)(2\eta+\eta') + \cdots, \qquad \eta'=\xi'-1, \qquad (29)$$

$$N^{-1}F = -\theta\log\theta - (1-\theta)\log(1-\theta) + \left(\frac{2}{3}\eta + \frac{1}{3}\eta'\right)\theta^2 +$$

$$+ \left(\frac{1}{3}\eta^2 + \frac{1}{6}\eta'^2\right)\theta^2(\theta^2-2\theta) + \left(\frac{2}{9}\eta^3 + \frac{1}{9}\eta'^3\right)[\theta^3 +$$

$$+ \theta^2(1-\theta)^2(-1-2\theta+2\theta^2)] + \frac{1}{3}\eta^2\eta'\theta^2(1-\theta)^2 + \cdots . \qquad (30)$$

We know that for this hypothetical lattice,

$$\Sigma \lambda_{cc'} = \frac{4}{3}N, \qquad \Sigma \mu_{cc'} = \frac{2}{3}N,$$
$$\Sigma \lambda_{cc'}\lambda_{cc''}\mu_{c'c''} = \frac{2}{3}N, \qquad \Sigma \cdots = 0, \cdots, \qquad (31)$$

and also that f_λ is expression (7), and $f_{\mu\mu}$ is expression (7) in which ξ is replaced by ξ' (η is replaced by η'). Substituting all of them into (27) and then comparing it with (30), we arrive at the result

$$f_{\mu\lambda}(\theta,T) = \frac{1}{2}\theta^2(1-\theta)^2\eta^2\eta' + \cdots . \qquad (32)$$

All the above calculations have shown the applicability of the method of reference 1 to any kind of solid solution. It is much more dependable, because it does not involve series expansion in $(kT)-1$ or (kT). Moreover, from the procedure shown above we can see that this method is much simpler in calculation.

PART II

QUASI-CHEMICAL FORMULAS

A very powerful way to treat quasi-chemical formulas is by the method of reference 1. We will consider two cases:

(1) The quasi-chemical formula of a multiple-component solid solution, neglecting all but one coordination number.

Denote the number of atoms of each component group by $N\theta_1, N\theta_2, \cdots,$. Here $\sum \theta_i = 1$. Denote the total number of permutations by M when we permute them on N points. Then the logarithm of the configurational partition function is equal to

$$\log M + (\sum \lambda_{cc'}) f_1(\theta_1, \theta_2, \cdots, T) + \cdots. \tag{33}$$

By ignoring the unwritten terms in the above expression, we will get the conventional quasi-chemical formula.
In order to determine f_1, we will discuss again the hypothetical lattice system (1) of Part I. Its F is

$$\frac{1}{2} N \log (\sum \lambda_i \lambda_j \xi_{ij}) - \sum N \theta_i \log \lambda_i, \tag{34}$$

$$\xi_{ij} = \exp(-V_{ij}/kT),$$

where the λ are determined by $\partial F / \partial \lambda_i = 0$ $i = 1, 2, \cdots$ i.e., they are determined by

$$\theta_i = \sum_j \lambda_i \lambda_j \xi_{ij} / \sum_{kl} \lambda_k \lambda_l \xi_{kl} \tag{35}$$

Now,

$$\sum_i \lambda_{cc'} = N, \qquad \sum \lambda \lambda \lambda = \sum \lambda \lambda \lambda \lambda = 0, \cdots,$$

Therefore, we have

$$N f_1(\theta_1, \theta_2, \cdots T) = \frac{1}{2} N \log (\sum \lambda_i \lambda_j \xi_{ij}) - \sum N \theta_i \log \lambda_i - \log M. \tag{36}$$

Substituting into (33), we get

$$F = (1 - N^{-1} \sum \lambda_{cc'}) \log M + (\sum \lambda_{cc'}) \left[\frac{1}{2} \log (\sum \lambda_i \lambda_j \xi_{ij}) - \sum \theta_i \log \lambda_i \right]. \tag{37}$$

where the λ's are functions of O and T, determined by expression (35). The number of pairs of nearest neighbors, X_{ij}, made up of atoms of the i-th kind and the j-th kind, is

$$\xi_{ij} \frac{\partial}{\partial \xi_{ij}} F\ (\xi_{11}, \xi_{12}, \cdots, \theta_1, \theta_2),\qquad ^{1)}$$

i.e.,

$$\xi_{ij}\partial F(\xi_{11}, \xi_{12}, \cdots, \lambda_1, \lambda_2, \cdots)\ \partial \xi_{ij}. \qquad (38)$$

Similarly, the number of pairs of nearest neighbors of i-th kind of atom is

$$\xi_{ii}\partial F/\partial \xi_{ii}.$$

Therefore,

$$\left. \begin{aligned} X_{ij} &= (\textstyle\sum \lambda_{\omega'})\lambda_i \lambda_j \xi_{ij},\ \textstyle\sum \lambda_k \lambda_l \xi_{kl}, \\ X_{ii} &= \tfrac{1}{2}(\textstyle\sum \lambda_{\omega'})\lambda_i^2 \xi_{ii}/\textstyle\sum \lambda_k \lambda_l \xi_{kl}. \end{aligned} \right\} \qquad (39)$$

Therefore,

$$X_{ij}^2/X_{ii}X_{jj} = 4 e^{-(2V_{ij} - V_{ii} - V_{jj})/kT}, \qquad (40)$$

This is what we want to prove. By a similar procedure, we can obtain the quasi-chemical formulas when the left side of (40) is $\dfrac{X_{ij}X_{jk}}{X_{jj}X_{ik}}$ or $\dfrac{X_{ij}X_{ki}}{X_{ii}X_{jj}}$.

From expression (40), it is very easy to calculate the total number of permutations obtained by permuting the atoms on the lattice, which produces all the atom pairs of all kinds, X_{11}, X_{12}, ..., etc. First, it can be derived from (40) that

$$N^{-1}\log g(N, \theta_1, \theta_2, \cdots, X_{11}, X_{12}\cdots) = \phi(N, \theta) - \sum_i X_{ii}\log X_{ii} - \sum_{i>j} X_{ij}\log \tfrac{1}{2}X_{ij}, \quad (41)$$

where $\phi(N,\theta)$ is a function to be determined. When

$$X_{ii} = \tfrac{1}{2}(\textstyle\sum \lambda_{\omega'})\theta_i^2, \qquad X_{ij} = (\textstyle\sum \lambda_{\omega'})\theta_i \theta_j \qquad (42)$$

the right side of expression (41) should be equal to $N \sum \theta_i \log \theta_i$, and therefore $\phi(N,\theta)$ can be termined. Now denoting the number of nearest neighbors of one point in the lattice, $N^{-1}\sum \lambda_{\omega'}$, by z, we would obtain

$$\log g(N, \theta_1, \theta_2, \cdots, X_{11}, X_{12}, \cdots) = N\sum (z-1)\theta_i \log \theta_i +$$
$$+ \tfrac{1}{2}Nz\log \tfrac{1}{2}Nz - \sum X_{ii}\log X_{ii} - \sum_{i>j} X_{ij}\log \tfrac{1}{2}X_{ij}. \qquad (43)$$

1) In carrying out this partial differentiation, ξ_{ij} and ξ_{ji} are treated as the same quantity, instead of as mutually independent variables.

If there is long-distance order, the quasi-chemical formula can also be derived by following the same prodecure. In fact, if we apply the method mentioned here to the AB-type lattice solid solution, we will obtain the conventional quasi-chemical formula immediately(no matter how many kinds of atoms there are).

(2) The quasi-chemical formula with higher coordination numbers included.

We are going to discuss the quasi-chemical formula when higher coordination numbers are included. For concreteness, we will consider only the case (2) of Part I, and discuss only the f_1 and f_3 terms (i.e., consider only $\sum\lambda$ and $\sum\lambda\lambda\lambda$ terms, and neglect all the other coordination numbers). We can prove that F is equal to

$$\log\binom{N}{N\theta}\left(1-\frac{\sum\lambda_{cc'}}{N}+\frac{\sum\lambda_{cc'}\lambda_{cc''}\lambda_{c'c''}}{2N}\right)+$$

$$+\left(\sum\lambda_{cc'}-\sum\lambda_{cc'}\lambda_{cc''}\lambda_{c'c''}\right)\left\{\frac{1}{2}\log\left(\lambda_A^2\xi_{AA}+2\lambda_A\lambda_B\xi_{AB}+\right.\right.$$

$$\left.\left.+\lambda_B^2\xi_{BB}\right)-\theta_A\log\lambda_A-\theta_B\log\lambda_B\right\}+$$

$$+\frac{1}{2}\sum\lambda_{cc'}\lambda_{cc''}\lambda_{c'c''}\left\{\frac{1}{3}\log\left(K_A^3\xi_{AA}^3+3K_A^2K_B\xi_{AA}\xi_{AB}+\right.\right.$$

$$\left.\left.+3K_AK_B^2\xi_{AB}\xi_{BB}+K_B^3\xi_{BB}^3\right)-\theta_A\log K_A-\theta_B\log K_B\right\}, \tag{44}$$

where $\lambda_A, \lambda_B,$ K_A and K_B are functions of θ and T, determined by

$$\frac{\partial}{\partial\lambda_A}=\frac{\partial}{\partial\lambda_B}\left\{\frac{1}{2}\log\left(\lambda_A^2\xi_{AA}+2\lambda_A\lambda_B\xi_{AB}+\lambda_B^2\xi_{BB}\right)-\theta_A\log\lambda_A-\theta_B\log\lambda_B\right\}=0,$$

$$\frac{\partial}{\partial K_A}=\frac{\partial}{\partial K_B}\left\{\frac{1}{3}\log\left(K_A^3\xi_{AA}^3+3K_A^2K_B\xi_{AA}\xi_{AB}+\cdots\right)-\theta_A\log K_A-\theta_B\log K_B\right\}=0. \tag{45}$$

From (44) and

$$X_{AA}=\xi_{AA}(\partial F/\partial\xi_{AA}),\quad X_{AB}=\xi_{AB}(\partial F/\partial\xi_{AB}),\cdots$$

the numbers X_{AA}, X_{AB} and X_{BB}, of AA, AB, BB near-neighbor pairs, can be easily determined. In fact, if we define

$$X'_{AA}=\frac{1}{2}\left(\sum\lambda-\sum\lambda\lambda\lambda\right)\frac{\lambda_A^2\xi_{AA}}{\lambda_A^2\xi_{AA}+2\lambda_A\lambda_B\xi_{AB}+\lambda_B^2\xi_{BB}},$$

$$X'_{AB}=\frac{1}{2}\left(\sum\lambda-\sum\lambda\lambda\lambda\right)\frac{\lambda_A\lambda_B\xi_{AB}}{\lambda_A^2\xi_{AA}+2\lambda_A\lambda_B\xi_{AB}+\lambda_B^2\xi_{BB}},\cdots,$$

$$X''\binom{A}{AA}=\frac{1}{6}\sum\lambda\lambda\lambda\frac{K_A^3\xi_{AA}^3}{K_A^3\xi_{AA}^3+3K_A^2K_B\xi_{AA}\xi_{AB}+3K_AK_B^2\xi_{AB}\xi_{BB}+K_B^3\xi_{BB}^3},$$

$$X''\binom{A}{AB}=\frac{1}{6}\sum\lambda\lambda\lambda\frac{K_A^2K_B\xi_{AA}\xi_{AB}}{K_A^3\xi_{AA}^3+3K_A^2K_B\xi_{AA}\xi_{AB}+\cdots},\cdots, \tag{46}$$

then we will have

$$X_{AA} = X'_{AA} + 3X''\binom{A}{AA} + 3X''\binom{A}{AB},$$

$$X_{AB} = 2X'_{AB} + 6X''\binom{A}{AB} + 6X''\binom{A}{BB},$$

$$X_{BB} = X'_{BB} + 3X''\binom{B}{BB} + 3X''\binom{A}{BB}, \tag{47}$$

and

$$\frac{(X'_{AB})^2}{X'_{AA}X'_{BB}} = \frac{\left[X''\binom{A}{AB}\right]^2}{X''\binom{A}{AA}X''\binom{A}{BB}} = \frac{\left[X''\binom{A}{BB}\right]^2}{X''\binom{B}{BB}X''\binom{A}{AB}}$$

$$= \exp\{-(2V_{AB} - V_{AA} - V_{BB})/kT\}, \tag{48}$$

$$2(X'_{AA} + X'_{AB}) = (\Sigma\lambda - \Sigma\lambda\lambda)\theta_A,$$
$$2(X'_{AB} + X'_{BB}) = (\Sigma\lambda - \Sigma\lambda\lambda)\theta_B, \tag{49}$$

$$3X''\binom{A}{AA} + 6X''\binom{A}{AB} + 3X''\binom{A}{BB} = \frac{1}{2}(\Sigma\lambda\lambda)\theta_A,$$

$$3X''\binom{B}{BB} + 6X''\binom{A}{BB} + 3X''\binom{A}{AB} = \frac{1}{2}(\Sigma\lambda\lambda)\theta_B. \tag{50}$$

Expressions (47), (48), (49) and (50) are the extended quasi-chemical formulas. We want to point out that X' can be found from (48) and (49), X" can be found from (48) and (50), and then we can calculate X. The influence of introducing more coordination numbers is exactly the same so we will not bother to show the development.

The number of permutations corresponding to X' and X" can easily be calculated from expressions (48) -- (50), but since the physical significances of X' and X" are ambiguous we do not make that calculation. For face-centered cubic system,

$$\Sigma\lambda = 12N, \qquad \Sigma\lambda\lambda = 48N,$$

so that X'_{AA} X'_{AB}, X'_{AB} X'_{BB} may assume negative values. Therefore they do not bear any direct physical significance.

We can see that, if we do not use the above-mentioned method but introduce X_{AA}^A directly to represent the number of atom groups containing three A atoms which form mutually nearest neighbors, and introduce also X_{AB}^A to represent the number of groups containing two A atoms and one B atom which form mutually nearest neighbors, etc., then we can extend the conventional quasi-chemical formula of the face-centered binary solid solution as follows:

$$\frac{\left[X\left({}^{A}_{AB}\right)\right]^2}{X\left({}^{A}_{AA}\right)X\left({}^{A}_{BB}\right)} = \frac{\left[X\left({}^{A}_{BB}\right)\right]^2}{X\left({}^{A}_{BB}\right)X\left({}^{B}_{BB}\right)} =$$

$$= 3\exp\{-(2V_{AB}-V_{AA}-V_{BB})\ kT\}, \tag{51}$$

$$3X\left({}^{A}_{AA}\right)+2X\left({}^{A}_{AB}\right)+X\left({}^{A}_{BB}\right)=24N\theta_A,$$

$$3X\left({}^{B}_{BB}\right)+2X\left({}^{B}_{BA}\right)+X\left({}^{A}_{AB}\right)=24N\theta_B. \tag{52}$$

(In the above expression, 24 N is equal to 1/2 $\Sigma\lambda\lambda\lambda$). In this theory, the numbers X_{AA}, X_{AB} and X_{BB} of AA, AB, and BB pairs of nearest neighbors are determined by the following expressions:

$$X_{AA}=\frac{1}{4}\left\{3X\left({}^{A}_{AA}\right)+X\left({}^{A}_{AB}\right)\right\},$$

$$X_{AB}=\frac{1}{4}\left\{2X\left({}^{A}_{AB}\right)+2X\left({}^{A}_{BB}\right)\right\},$$

$$X_{BB}=\frac{1}{4}\left\{3X\left({}^{B}_{BB}\right)+X\left({}^{B}_{BA}\right)\right\}. \tag{53}$$

On comparing this theory with expressions (47)-(50), we must note that the expressions here

$$X\left({}^{A}_{AB}\right), \ X\left({}^{A}_{BB}\right)$$

correspond to

$$3X''\left({}^{A}_{AB}\right), \ 3X''\left({}^{A}_{BB}\right).$$

Therefore, in both theories, the parts involving

$$X\left({}^{A}_{AA}\right), \ X\left({}^{A}_{AB}\right), \ X\left({}^{A}_{BB}\right), \ X\left({}^{B}_{BB}\right)$$

are identical. But expression (53), for determining X_{AA}, etc., is essentially different from (47). Expression (53) has a factor of 1/4 on its right side, arising from the fact that one pair of nearest neighbors exists for every

four atom groups, each group containing three atoms form-
ing mutually nearest neighbors. In expression (47), we
do not have a factor corresponding to this. Finally, we
will derive the number of combination g, of

$$X\binom{A}{AA}, \ X\binom{A}{AB}, \ X\binom{A}{BB}, \ X\binom{B}{BB}$$

corresponding to N, Θ_A, Θ_B.

Suppose log g takes the following form:

$$-c_1(X_{AAB}\log X_{AAB}+X_{ABB}\log X_{ABB})-c_2(X_{AAA}\log X_{AAA}+$$
$$+X_{BBB}\log X_{BBB})+c_3(X_{AAB}+X_{ABB})+c_4(X_{AAA}+X_{BBB})+\phi(N,\theta), \qquad (54)$$

where X_{AAA}, X_{AAB},..., i.e., X_{AA}^{A}, X_{AB}^{A}, ..., c_1, c_2, c_3, c_4,
are constants to be determined and $\phi(N,\theta)$ is a function to
be determined.

Treating the configurational free energy as a function of N,
$\theta_A, \theta_B, X_{AAB}, X_{ABB}$., (so that we can put $c_4=0$), and setting its de-
rivatives with respect to X_{AAB}, X_{ABB} equal to zero, we
obtain

$$-c_1\log X_{AAB}-c_1+\frac{2}{3}c_2\log X_{AAA}+\frac{2}{3}c_2+\frac{1}{3}c_2\log X_{BBB}$$

$$+\frac{1}{3}c_2+c_3+(-2V_{AB}+V_{AA}+V_{BB})/kT=0,$$

$$-c_1\log X_{ABB}-c_1+\frac{2}{3}c_2\log X_{BBB}+\cdots=0, \qquad (55)$$

But from (51), we have

$$(-2V_{AB}+V_{AA}+V_{BB})/kT=\log\frac{3 X_{AAB}^2}{X_{AAA}X_{ABB}}=\log\frac{3 X_{ABB}^2}{X_{BBB}X_{AAB}},$$

i.e.,

$$(-2V_{AB}+V_{AA}+V_{BB})/kT=\frac{1}{3}\log\frac{27 X_{AAB}^3}{X_{AAA}^2 X_{BBB}}, \qquad (56)$$

Substituting into the first expression of (55), we get

$$c_1=1, \qquad c_2=1, \qquad c_3=\log 3. \qquad (57)$$

And by the same time, the second equation of (55) is also
satisfied. Therefore, expression (54) is proved to be the
exact expression of log g, and it is also equal to

$$\log g=\phi(N,\theta)-X_{AAB}\log\frac{1}{3}X_{AAB}-X_{ABB}\log\frac{1}{3}X_{ABB}$$

$$-X_{AAA}\log X_{AAA}-X_{BBB}\log X_{BBB}, \qquad (58)$$

— 15 —

an expression very similar to (41).
When

$$X_{AAA} = \frac{1}{3} N \cdot 24 \theta_A^3, \qquad X_{AAB} = N \cdot 24 \theta_B \theta_A^2,$$

$$X_{BBA} = N \cdot 24 \theta_A \theta_B^2, \qquad X_{BBB} = \frac{1}{3} N \cdot 24 \theta_B^3$$

log g should be equal to $N \theta_A \log \theta_A - N \theta_B \log \theta_B$, and then we have

$$\phi(N, \theta) = -N \theta_A \log \theta_A - N \theta_B \log \theta_B +$$
$$+ \frac{1}{3} \sum \theta_1 \theta_2 \theta_3 N \cdot 24 \log \frac{1}{3}(N \cdot 24 \theta_1 \theta_2 \theta_3),$$

where the summation is taken over θ_1, θ_2 and θ_3, and each
of $\theta_1, \theta_2, \theta_3$ can assume two values, θ_A, θ_B . Therefore

$$\phi(N, \theta) = -N \theta_A \log \theta_A - N \theta_B \log \theta_B + 8N \log 8N + \sum \theta_1 \theta_2 \theta_3 N \cdot 24 \log \theta_1 =$$
$$= -N \theta_A \log \theta_A - N \theta_B \log \theta_B + 8N \log 8N + N 24(\theta_A \log \theta_A + \theta_B \log \theta_B). \quad (59)$$

Substituting into (58), we obtain the desired result:

$$\log g = 8N \log 8N + 23 N(\theta_A \log \theta_A + \theta_B \log \theta_B) -$$
$$- X_{AAA} \log X_{AAA} - X_{BBB} \log X_{BBB} - X_{AAB} \log \frac{1}{3} X_{AAB} - X_{ABB} \log \frac{1}{3} X_{ABB}. \quad (60)$$

Undoubtedly, this treatment can be extended to the
face-centered lattice solid solution of multiple components.
The result corresponding to (60) is

$$\log g = 8N \log 8N + 23 N \sum \theta_i \log \theta_i$$

$$- \sum_i X_{iii} \log X_{iii} - \sum_{i>j} \left[X_{iij} \log \frac{1}{3} X_{iij} + \right.$$
$$+ X_{ijj} \log \frac{1}{3} X_{ijj} \left.\right] - \sum_{i>j>k} X_{ijk} \log \frac{1}{6} X_{ijk}. \quad (61)$$

All the notations in this expression follow the usual conven-
tion, and $X_{iii}, X_{ijj}, X_{ijk}$ and X_{ii}, X_{ij}, have the following
relations:

$$3 X_{iii} + \sum_j (X_{iij} + 2 X_{iij}) + \sum_{j>k} X_{ijk} = 24 N \theta_i,$$

$$X_{ii} = \frac{1}{4} \left(3 X_{iii} + \sum_j X_{iij} \right),$$

$$X_{ij} = \frac{1}{4} \left(2 X_{iij} + 2 X_{ijj} + \sum_k X_{ijk} \right). \quad (62)$$

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